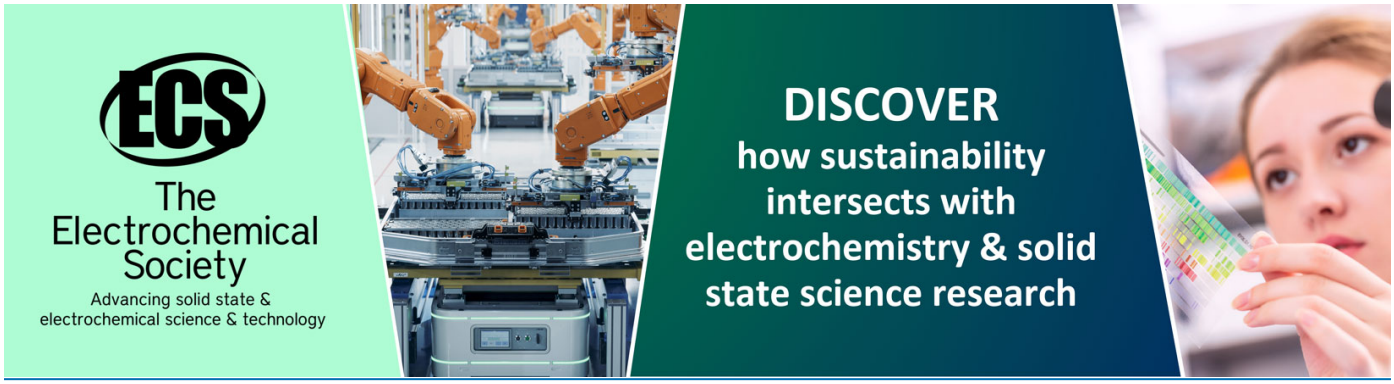
Dielectric properties of ferroelectric diisopropylammonium bromide embedded in porous glass



Dielectric properties of ferroelectric diisopropylammonium bromide embedded in porous glass

A Yu Milinskiy[1], S V Baryshnikov[1,2], E V Charnaya[3] and N I Uskova[3,4]

[1] Blagoveschensk State Pedagogical University, Blagoveschensk, 675000, Russia;
[2] Amur State University, Blagoveshchensk, 675027, Russia
[3] St. Petersburg State University, St. Petersburg, 199034, Russia
[4] St. Petersburg State University of Aerospace Instrumentation, St. Petersburg, 190000, Russia

e-mail: a.milinskiy@mail.ru

Abstract. The results of studying the dielectric constant ε′ and the third harmonic coefficient $\gamma_{3\omega}$ of a new organic ferroelectric diisopropylammonium bromide ($C_6H_{16}NBr$, DIPAB), embedded in porous glasses with an average pore size of 100 nm are presented. Diffusion and shifting of the phase transition to low temperatures by 5 K were detected in comparison with bulk DIPAB. A decrease in the phase transition temperature in nanocomposites with DIPAB nanoparticles is qualitatively consistent with theoretical models of the size effects on the structural phase transition.

1. Introduction

Ferroelectrics are multifunctional materials with a wide range of applications. Their temperature-dependent spontaneous polarization and dielectric constant can change under the influence of an electric field or mechanical stresses, which makes them attractive for creating various electronic devices. At present, ferroelectric materials with high functional parameters, that are environmentally friendly and at the same time cheap and light, are being actively searched. In recent years, several organic ferroelectrics, belonging to the $C_6H_{16}NA$ salt family, have been discovered, where A denotes Cl, Br, and I [1-3]. Such ferroelectrics include diisopropylammonium chloride (DIPAC) $P_s \sim 8.2$ μC × cm^{-2}, $T_c = 440$ K [1]; diisopropylammonium bromide (DIPAB) $P_s \sim 23$ μC × cm^{-2}, $T_c = 426$ K [2]; diisopropylammonium iodide (DIPAI) $P_s \sim 5.17$ μC × cm^{-2}, $T_c = 378$ K [3].

The highest spontaneous polarization, comparable to one of $BaTiO_3$, is demonstrated by DIPAB, which makes it a potential material for application in micro and nanoelectronics. Connected with the prospects for the practical use of new organic ferroelectrics, studies of the effect of downsizing on their properties are of considerable interest. Phase transitions in nanocomposites, based on DIPAC in an opal matrix and DIPAB in porous Al_2O_3 films, were investigated in [4–6]. Temperature shifts and a change in the sequence of ferroelectric phase transitions were detected.

This paper presents the results of studying the linear and nonlinear dielectric properties of DIPAB, embedded in porous glasses with an average pore size of 100 nm, compared to the properties of bulk DIPAB.

2. Samples and experimental procedure

Diisopropylammonium bromide was obtained by the reaction of diisopropylamine with a 48% aqueous solution of HBr (1:1 molar ratio), according to the procedure, given in [2], followed by

recrystallization from methyl alcohol at room temperature. According to the XRD spectrum, at room temperature DIPAB has a $P2_1$ structure (CCDC card No. 770675).

To obtain the nanocomposites, we used porous glass with an average pore size of 100 nm and a porosity of 48.8%. The ferroelectric was introduced into the pores from a heated saturated solution of $C_6H_{16}NBr$ in methanol. Then, the solution with the sample was slowly cooled, this resulted in nucleation of nanocrystals in the pores, that had been growing for several days. Vacuum drying was used to remove the remaining methanol. The described procedure was repeated three times. The degree of filling of the pores, determined by the change in the film mass, the AND BM-252G balance being used, was not less than 50%.

To measure the complex permittivity, we used an E7–25 digital immitance meter with a frequency range of $20 \div 10^6$ Hz and an operating voltage of 0.7 V. In-Ga paste was used as electrodes. The temperature was determined, using an electronic thermometer TS-6621 with a chromel-alumel thermocouple. The accuracy of determining the temperature was 0.1 K. The studies were carried out in the heating and cooling mode at a rate of 1 K per minute in the temperature range 300-440 K.

The setup for studying the nonlinear dielectric properties of samples included a harmonic oscillator with an operating frequency of 2 kHz. During the measurement, the electric field strength, applied for the bulk and nanocomposite DIPAB, was about 50 and 100 V/mm, respectively. During the experiment, the amplitudes of the third harmonic and the main signal were recorded. The nonlinear measurement technique is described in more detail in [7].

3. Experimental results and discussion

In ferroelectrics, when an electric field E is applied, no coercive polarization switching occurs. For a uniaxial ferroelectric with homogeneous polarization the electrical displacement D can be decomposes in a power series E [8, 9]:

$$D = P_s + \varepsilon \frac{\partial P}{\partial E} E + \frac{1}{2}\varepsilon^2 \frac{\partial^2 P}{\partial E^2} E^2 + \frac{1}{6}\varepsilon^3 \frac{\partial^3 P}{\partial E^3} E^3 + ... + \frac{1}{n!}\varepsilon^n \frac{\partial^n P}{\partial E^n} E^n = \\ = P_s + \varepsilon_1 E + \varepsilon_2 E^2 + \varepsilon_3 E^3 ..., \quad (1)$$

where P_s is spontaneous polarization, the coefficient ε1 denotes linear permittivity, and ε_2 and ε_3 are permittivities of the second and third orders, respectively. As a result of the nonlinear dependence of D on E, when an electric field is applied to the sample, changing according to the law $E = E_0\sin(\omega t)$, higher harmonics will be present in the current through the resistor at frequencies 2ω, 3ω, ... which amplitudes will be proportional to ε_2 and ε_3, ... respectively. In the paper, we study the third harmonic coefficient of temperature behavior $\gamma_{3\omega} = (u_{3\omega}/u_\omega)$ – the ratio of the amplitude of the third harmonic to the amplitude of the main signal

As shown in [9], the current of the third harmonic for the ferroelectrics with a first-order phase transition will be determined by the relation:

$$I_{3\omega} = 3\left(\omega S \chi^4 \frac{U_o^3}{h^3}\right)\left[\left(\beta + 10\gamma P_s^2\right) + \frac{5}{2}\omega S \frac{U_o^2}{h^2}\gamma\chi^2\right]\cos(3\omega t). \quad (2)$$

Given the expression for I_ω

$$I_\omega = \left(\omega\chi \frac{U_o}{h}\right)\sin(\omega t),$$

we obtain the third harmonic coefficient $\gamma_{3\omega} = I_{3\omega}/I_\omega$,

$$\gamma_{3\omega} = 3\left(\chi^3 \frac{U_o^2}{h^2}\right)\left[\left(\beta + 10\gamma P_s^2\right) + \frac{5}{2}\omega S \frac{U_o^2}{h^2}\gamma\chi^2\right] \quad (3)$$

where χ is dielectric susceptibility, P_s is the spontaneous polarization, β and γ are the Landau expansion coefficients, and S and h are the sample dimensions. It follows from (3), that the coefficient of the third harmonic $\gamma_{3\omega}$ increases significantly in the polar phase due to the appearance of spontaneous polarization and has a minimum at the phase transition point due to the vanishing of P_s.

Thus, the study of the temperature dependence of the third harmonic generation is a convenient method of recording a ferroelectric state.

The temperature dependences of the real part of the dielectric constant ε′ for bulk DIPAB samples, obtained in the heating and cooling mode, are shown in Fig. 1. The maxima in the ε′(*T*) curves are observed at a temperature of 425.8 K, which corresponds to the $P2_1 \rightarrow P2_1/m$ structural transition [2]. Upon cooling, the maximum ε′ shifts toward low temperatures by about 3 K. The temperature hysteresis is due to the first-order phase transition.

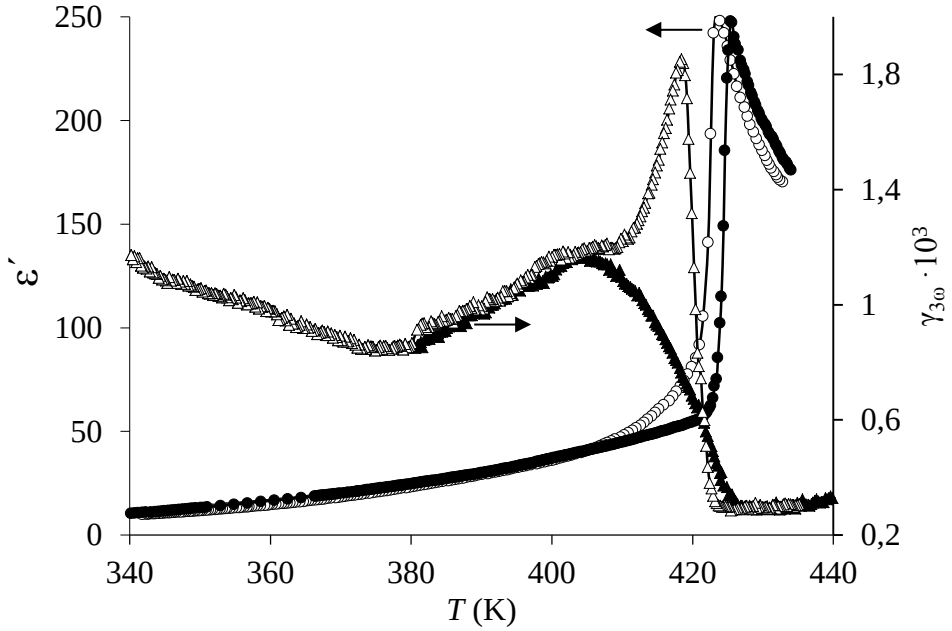


Figure 1. Temperature dependences of the material part of the dielectric constant ε′ at a frequency of 1 kHz (circles) and the third harmonic coefficient $\gamma_{3\omega}$ (triangles) for a pressed polycrystalline DIPAB sample. Filled symbols correspond to heating, unfilled symbols correspond to cooling.

Figure 2 presents the temperature dependences of the real part of the dielectric constant ε′ for porous glasses, filled with DIPAB, obtained in the heating and cooling mode. Dielectric anomalies in the phase transition region for nanocomposites are less pronounced in comparison with the bulk samples. The diffused anomalies on the ε′(*T*) curves correspond to the phase transition. The activation increase in the dielectric constant in nanocomposites is apparently due to the contribution of the Maxwell – Wagner polarization [10], which arises because of the redistribution of charge density at the boundaries between porous glass and DIPAB inclusions.

Figure 2 shows that the anomaly of the dielectric constant during heating, associated with the ferroelectric phase transition in nanocomposites, is shifted toward low temperatures by 5 K (T_c = 421 K), as compared to the bulk sample. We also note, that along with a decrease in the phase transitions temperature and a significant blurrings of transitions, the temperature hysteresis of the phase transition in nanocomposites increases, which indicates an increase in the DIPAB primordiality under conditions of limited geometry. The temperature of the phase transition in the cooling mode, determined from the maximum dielectric constant, is about T_c = 413 K.

To establish the temperature range of the ferroelectric phase existence, the nonlinear dielectric properties of bulk DIPAB and DIPAB in porous glass were studied. Figures 1 and 2 present the temperature dependences of the third harmonic coefficient $\gamma_{3\omega}$ of the samples, studied during the first pass, obtained upon heating and cooling. According to the results, obtained upon samples heating, high values of the coefficient $\gamma_{3\omega}$ for bulk and nanocomposite DIPAB are observed from room temperature to 426 and 421 K, respectively. Above these temperatures, the coefficient of the third harmonic changes insignificantly, which is associated with the presence of samples in the paraelectric

state. Upon samples cooling, the growth of the coefficient $\gamma_{3\omega}$ begins at around 423 and 413 K for bulk and nanocomposite DIPAB, respectively.

In interpreting the temperature shift of the phase transition for nanoparticles under conditions of nanoconfinement, as a rule, we use size effect models, developed for isolated particles, based on the Landau phenomenological theory and the Ising model [11, 12]. They predict that the temperature of the structural phase transition should decrease with decreasing particle size if the order parameter or the value of the exchange integral at the particle boundaries is less than in the particles volume. However, for particles in the matrices, an interaction with pore walls and interaction between particles in neighboring pores can also lead to a shift in the temperature of the phase transition [13, 14]. Moreover, depending on the geometry of the pore network and the shape of the particles, such an interaction can change the influence of size effects, leading to both an increase and decrease in the transition temperature.

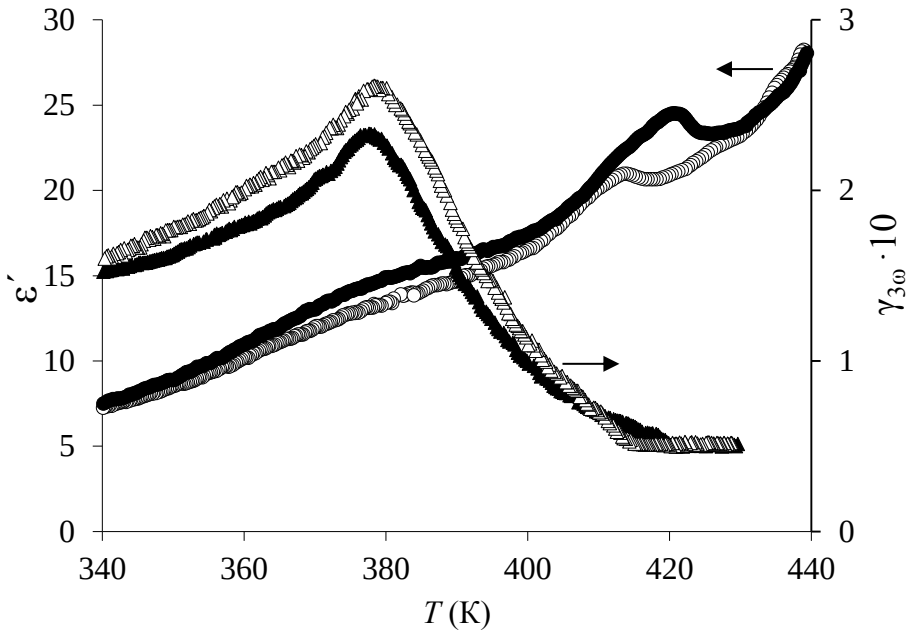


Figure 2. Temperature dependences of the material part of the dielectric constant ε´ at a frequency of 1 kHz (circles) and the third harmonic coefficient $\gamma_{3\omega}$ (triangles) for porous glass, filled with DIPAB. Filled symbols correspond to heating, unfilled symbols correspond to cooling.

Previous studies of nanocomposites, which are porous alumina films with DIPAB inclusions, revealed a decrease in the Curie temperature with a decrease in pore size [5]. So, at an Al_2O_3 pore size of 100 nm, the Curie temperature decreased by 5 ± 1 K. Thus, it can be assumed that the shift in the temperature of the DIPAB phase transition in porous glass is mainly determined by size effects, as well as for a separate isolated particle. This is supported by the same change in the Curie temperature for nanocomposites, obtained on the basis of various porous matrices (Al_2O_3, porous glass) with DIPAB inclusions. The question of the phase transition blurring in nanoscale matrices is not a new one; it was theoretically posed earlier in a number of works [15, 16]. Among the reasons that can lead to this effect, are the inhomogeneous distribution of deformations for particles in the pores and the magnitude of the effective internal electric field. A similar picture is also observed in bulk disordered ferroelectric structures and solid solutions.

4. Conclusion

Thus, in this work, dielectric studies of diisopropylammonium bromide, embedded in porous glasses, were carried out. The studies revealed a Curie temperature shift to low temperatures of 5 K and an increase in temperature hysteresis of 5 K for DIPAB in porous glass, compared to a bulk sample. The

lowering of the phase transition temperature can be interpreted on the basis of known theoretical models for ferroelectric small particles.

Acknowledgements
This work was supported by the Russian Foundation for Basic Research, Project No. 19-29-03004.

References

[1] Fu D W, Zhang W, Cai H L, Ge J Z, Zhang Y and Xiong R G 2011 *Adv. Mater.* **23** 5658
[2] Fu D W, Cai H L, Liu Y, Ye Q, Zhang W, Zhang Y, Chen X Y, Giovannetti G, Capone M, Li J, and Xiong R G 2013 *Science* **339** 425
[3] Saripalli R K, Diptikanta S, Prasad S, Nhalil H, Bhat H L, Guru Row T N, Suja E 2017 *J. Appl. Phys.* **121** 114101
[4] Baryshnikov S V, Charnaya E V, Milinskiy A Yu, Parfenov V A, Egorova I V 2018 *Phase Trans.* **91** 293
[5] Milinskii A Y, Baryshnikov S V, Charnaya E V, Egorova I V, Nguyen H T 2019 *J. Phys: Condens. Matter* **31** 485704
[6] Uskova N I, Charnaya E V, Podorozhkin D Yu, Baryshnikov S V, Milinskiy A Yu, Egorova I V, Nefedov D Yu 2020 *Appl. Magn. Reson.* **51** 129
[7] Milinskii A Yu, Baryshnikov S V, Parfenov V A, Kozlola S A, Thuong N H. 2018 *Transactions on Electrical and Electronic Materials* **19** 201
[8] Ikeda S, Kominami H, Koyama K, Wada Y 1987 *J Appl. Phys.* **62** 3339
[9] Yudin S G, Blinov L M, Petukhova N N, Palto S P 1999 *Journal of Experimental and Theoretical Physics Letters* **70** 633
[10] Wagner K W 1924 *Die Isolierstoffe der Elektrotechnik* (Berlin: Springer)
[11] Zhong W L, Wang Y G, Zhang P L, Qu B D 1994 *Phys. Rev.* B **50** 698
[12] Wang C L, Xin Y, Wang X S, Zhong W L 2000 *Phys. Rev.* B **62** 11423
[13] Uskov A V, Charnaya E V, Pirozerskii A L, Bugaev A S 2015 *Ferroelectrics* **482** 70
[14] Baryshnikov S V, Charnaya E V, Stukova E V, Milinskiy A Yu, Tien C 2010 *Phys. Solid State* **52** 1444
[15] Tagantsev A K 1997 *Integr. Ferroelectrics* **16** 237
[16] Zhong W L, Wang Y G, Zhang P L, Qu B D 1994 *Phys. Rev.* B **50** 698